

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C09C 1/30, C01B 33/18	A1	(11) International Publication Number: WO 99/36479 (43) International Publication Date: 22 July 1999 (22.07.99)
(21) International Application Number: PCT/US99/00157 (22) International Filing Date: 13 January 1999 (13.01.99) (30) Priority Data: 60/071,546 15 January 1998 (15.01.98) US (71) Applicant: CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US). (72) Inventors: MENON, Vinayan, C.; 801 Locust Place N.E. #2060 H, Albuquerque, NM 87102 (US). PAUL, Joanne; 1025 Valencia #12, Albuquerque, NM 87108 (US). SMITH, Douglas, M.; 215 Richmond S.E., Albuquerque, NM 87106 (US). KOEHLERT, Kenneth, C.; 1210 Dorchester Drive, Champaign, IL 61821 (US). (74) Agent: LANDO, Michelle, B.; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD OF PREPARING ORGANICALLY MODIFIED SILICA		
(57) Abstract		
<p>The present invention provides a method of preparing lipophilic silica in an aqueous medium in the absence of added acids, bases, or organic solvents. In particular, the present inventive method of preparing lipophilic silica comprises (a) providing a mixture consisting essentially of (i) at least one organically modified silica precursor which is a trifunctional silane, (ii) water, and (iii) at least one tetrafunctional silane, (b) allowing the organically modified silica to form in the mixture, and (c) removing the organically modified silica from the mixture.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

METHOD OF PREPARING ORGANICALLY MODIFIED SILICA

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a method of
5 preparing organically modified in an aqueous medium.

BACKGROUND OF THE INVENTION

Amorphous silica particles can be used as fluid
thickeners, thermal insulation, anti-caking agents,
10 molecular sieve materials, and reinforcing fillers for
silicone and rubber. The silica particles used for these
purposes have physical properties (e.g., particle size,
surface area, density, and surface polarity) that vary
according to the particular application.

15 For example, it is known that when silica particles
are to be used as fillers in silicone rubber formulations,
they become increasingly reinforcing as their sizes
diminish. It is further known that the undesirable
phenomenon of "crepe hardening" in filler applications can
20 be avoided if the silica particles have been organically
modified to make their surfaces hydrophobic or lipophilic.
This can be accomplished by any number of procedures, but
generally involves transforming some of the hydrophilic
silanol groups into hydrophobic silyl ethers. This
25 process occurs according to the general equation: $\text{Si-OH} +$
 $\text{R-LG} \rightarrow \text{Si-OR} + \text{H-LG}$, wherein R is an aromatic or
aliphatic hydrocarbon-containing moiety, such as
trimethylsilyl, and LG is a leaving group, such as
chloride. This procedure is commonly referred to as
30 "hydrophobing", "treating", or "capping" the silica, and
the organic reagents used for this purpose are called
hydrophobing, treating, or capping agents.

Hydrophobing reactions are typically performed in
the presence of organic co-solvents at either low or high
35 pH. For example, U.S. Patent 2,786,042 (Iler) discloses

the conversion of a silica hydrosol to a lipophilic silica organosol. The method comprises reacting the hydrosol with a hydrophobing agent, such as a chlorosilane, under acidic conditions in the presence of a cosolvent such as tert-butyl alcohol. A brine-immiscible organic solvent is then added while the pH is maintained at approximately 2 to 3 to prepare the organosol, from which the lipophilic silica may be obtained after drying.

In U.S. Patent 3,122,520 (Lentz), a silica hydrosol is again converted to a lipophilic silica organosol, but under more acidic conditions. In particular, a pH of less than about 1 is maintained during the reaction of the hydrosol with a chlorosilane or siloxane, and the subsequent preparation of the organosol is also conducted in the presence of a strong acid catalyst. The hydrophobed silica then can be obtained by boiling off the organic solvent.

The above procedures are indirect in that they use silica hydrosols as starting materials, which are made from silica and water. The silica, in turn, is made from another starting material (e.g., a chlorosilane), and the hydrophobing reaction takes place only after the execution of these preliminary steps. Furthermore, these procedures suffer from the fact that exogenous acids and organic solvents are used in the hydrophobing reactions, which adds cost and complexity to the overall process.

The most common source of silica for such reactions is that obtained via acidification of a solution of a sodium silicate. Alternatively, silica can be formed by burning SiCl_4 in the presence of methane or hydrogen to produce SiO_2 , H_2O , and HCl . Silica prepared by these methods is completely oxygenated (e.g., SiO_2) and is extremely hydrophilic. Significant quantities of hydrophobing agent are therefore required in order to satisfactorily increase the lipophilicity of the silica

for use in applications such as fillers for silicone rubber.

A direct method for preparing organically modified silica suitable for use as a silicone rubber filler is described in U.S. Patent 4,344,800 (Lutz). This patent teaches the use of an alkyl orthosilicate (e.g., methyl orthosilicate) as a starting material instead of a silica hydrosol. The alkyl orthosilicate is mixed with water, an alcohol, a basic catalyst, and a hydrophobing agent, aged for a period of time, and then filtered and/or oven-dried to provide the filler material. In this process, the silica is prepared in situ from the alkyl orthosilicate and treated in one step. However, it requires the use of an expensive orthosilicate, a basic catalyst, an organic solvent, and a significant quantity of a hydrophobing agent.

A need exists for a simple method of preparing organically modified silica that uses inexpensive processes and starting materials, as well as a reduced quantity of a hydrophobing agent. Furthermore, the method should not require the use of exogenous acids, bases, or organic solvents, but should have the flexibility to provide silica particles in a range of hydrophobicities or lipophilicities, surface areas, densities, etc. The present invention provides such a method.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to a method of preparing organically modified or lipophilic silica in an aqueous medium in the absence of added acids, bases, or organic solvents. In particular, the method comprises contacting a trifunctional silane such as methyltrichlorosilane, with water and a tetrafunctional silane such as silicic acid. One or more hydrophobing agents, such as trimethylchlorosilane and

hexamethyldisiloxane, also can be added to the mixture. According to the method of the present invention, using a trifunctional silane as a starting material allows organically modified silica to be produced from
5 inexpensive silica precursors and allows lipophilic silica to be produced using a reduced amount of hydrophobing agent. Moreover, both products (organically modified silica and, the more hydrophobic, lipophilic silica) optionally can be produced in the absence of a
10 organic cosolvents. The tetrafunctional silane imparts improved physical properties (e.g., lower density and larger surface area) to the lipophilic silica. No acids, bases, or external catalysts of any kind are required in the reaction mixture, and the method allows for the
15 production of hydrophobic silica particles in a wide range of surface areas, densities, and hydrophobicities or lipophilicities.

These and other advantages of the present invention, as well as additional inventive features, will be apparent
20 from the description of the invention provided herein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a method of preparing organically modified silica that is performed
25 in an aqueous medium and which can be performed in the absence of added acids, bases, or organic solvents. Organically modified silica prepared under some embodiments of the present invention is sufficiently hydrophobic, such that it is lipophilic. In particular,
30 the present inventive method of preparing organically modified silica comprises (a) providing a mixture consisting essentially of (i) at least one organically modified silica precursor which is a trifunctional silane, (ii) water, and (iii) at least one
35 tetrafunctional silane, (b) allowing the organically

modified silica to form in the mixture, and (c) removing the organically modified silica from the mixture.

By a trifunctional silane is meant a substituted silicon compound of the general formula RSiX_3 , wherein R is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less (e.g., methyl, trifluoromethyl, ethyl, pentafluoroethyl, propyl, butyl, isopropyl, tert-butyl, amyl, etc.) and phenyl radicals (e.g., phenyl, tolyl, fluorophenyl, chlorophenyl, nitrophenyl, hydroxyphenyl, etc.), and each X is independently selected from the group consisting of halogen radicals (e.g., chloro, bromo, iodo, etc.), and hydroxyl radicals and salts thereof (e.g., OH, O-Li, O-Na, O-K, etc.). The trifunctional silanes of the present invention react with water to provide oxygen-substituted silicon compounds of the general formula $\text{RSi(OH)}_x\text{O}_{1.5-x/2}$, wherein x is a number from 0 to 3, inclusive, and R is as previously defined.

According to the method of the present invention, preferred trifunctional silanes include chlorosilanes of the general formula RSiCl_3 , wherein R is as previously defined. An especially preferred chlorosilane is methyltrichlorosilane (CH_3SiCl_3 , MTCS). MTCS is a by-product of silicone precursor production, and as such is inexpensive and readily available.

The silica produced according to the present inventive method possesses an R group attached to silicon, as described above, and is therefore more lipophilic than conventional, fully oxygen-substituted silica (SiO_2). Organically modified silica of the present invention has a greater affinity for lipids, and a lesser affinity for water as compared to conventional silica. The lipophilicity of the inventive silica can be qualitatively measured by evaluating its solubility in a

mixture of methanol and water. Organically modified silicas prepared by the present inventive method preferably will have a BET C value of less than about 100, more preferably less than about 80, and optionally less than about 60, but need not float on water. Lipophilic silicas prepared according to the present inventive method will float on the top of the water, preferably for at least 200 hours. Preferably, a lipophilic silica will have a BET C value of less than about 40. More preferably, a lipophilic silica will have a BET C value of less than about 10. Typically, lipophilic silica can be wet by adding methanol to the water. Wetted (lipophilic) silica usually does not float on water.

A significant advantage of producing organically modified or lipophilic silica according to the method of the present invention compared to conventional methods of producing organically modified silica is that a selected level of organic treatment (or hydrophobicity) can be attained using a lower quantity of hydrophobing agent.

A hydrophobing agent in the context of the present invention is a compound that is capable of attaching an aliphatic hydrocarbon radical, aliphatic fluorocarbon radical, or a phenyl radical to a silanol group. Attachment of these organic radicals to the silica matrix reduces the hydrophilicity (i.e., increases the hydrophobicity) of the silica. This process occurs according to the general equation: $\text{SiO-H} + \text{R-LG} \rightarrow \text{SiO-R} + \text{H-LG}$, wherein R-LG represents a hydrophobing agent, SiO-H represents any silanol-containing molecule (e.g., silica), R is an aromatic or aliphatic carbon-containing moiety, such as trimethylsilyl, and LG is a leaving group, such as chloride.

Although the method of the present invention does not require the use of hydrophobing agents, any suitable

hydrophobing agent can be used to increase the lipophilicity of the inventive silica. Preferred are cyclic siloxanes of the general formula $(R_2SiO)_y$, linear siloxanes of the general formula $R'_3Si-O-(Si(R_2)-O)_z-SiR'_3$, monofunctional silanes of the general formula R_3SiX , and bifunctional silanes of the general formula R_2SiX , wherein each R' is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less (e.g., methyl, trifluoromethyl, ethyl, pentafluoroethyl, propyl, butyl, isopropyl, tert-butyl, amyl, etc.), phenyl radicals (e.g., phenyl, tolyl, fluorophenyl, chlorophenyl, nitrophenyl, hydroxyphenyl, etc.), and hydroxyl radicals, each R is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less and phenyl radicals, each X is independently selected from the group consisting of halogen radicals (e.g., chloro, bromo, iodo, etc.), y is 3 or 4, and z is an integer from 1 to 10, inclusive. Trimethylchlorosilane (TMCS), Diethyldichlorosilane (DECS), hexamethyldisiloxane (HMDS), octamethyltrisiloxane, decamethyltetrasiloxane, hexamethylcyclotrisiloxane, hydroxy terminated polydimethylsiloxane, and octamethylcyclotetrasiloxane are highly preferred hydrophobing agents.

The use of hydrophobing agents in accordance with the present inventive method, either during the formation reaction, or, preferably, during the recovery of the silica product from the aqueous mixture in which the silica is produced, enables the preparation of an organically modified silica that is a lipophilic silica. Preferably, the hydrophobing agent used to prepare a lipophilic silica incorporates into the silica matrix (1) a sterically-bulky organic radical (e.g., a radical comprising an isopropyl, tert-butyl, or aryl structure),

(2) two organic radicals comprising 3 to 6 carbon atoms each, or (3) a trialkyl silicon radical, wherein the alkyl groups are independently selected and can each comprise no more than 6 carbon atoms. Preferably, the hydrophobing agent is a monofunctional trialkylsilane of the formula $(R'')_3SiX$, wherein R'' is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less and X is as previously defined. A particularly preferred monofunctional trialkylsilane is trimethylchlorosilane.

By the level of organic treatment is meant the total number of carbon atoms that are attached to the silica (e.g., via chemical bonds). According to the present inventive method, in water the trifunctional silane comprises silica molecules with carbon atoms already attached thereto (i.e., the R groups in $RSi(OH)_xO_{1.5-x/2}$, wherein R and x are as previously defined) before any exogenous hydrophobing agent is added. Thus, the quantity of hydrophobing agent that must be subsequently added compared to conventional, fully oxygenated silica (i.e., SiO_2) to attain the same level of treatment is reduced.

A tetrafunctional silane is included in the method of the present invention to improve the physical properties (e.g., decrease density and increase surface area) of the organically modified silica produced in accordance with the present invention. Organically modified silica particles produced from a trifunctional silane alone have a tendency to possess high densities and low surface areas. As organically modified silica particles with low densities and high surface areas are preferred for use in many applications (e.g., reinforcing fillers for silicone rubber), it is often desirable to avoid the formation of dense particles that tend to

result when silica is produced from trifunctional silanes. Without intending to be bound by any particular theory, it is believed that porous, organically modified silica particles derived from trifunctional silanes have an inferior structural rigidity as compared to silica produced from tetrafunctional silanes. The trifunctional silane-derived organically modified silica therefore has a tendency to collapse when solvent is removed from its pores, resulting in dense particles as described above.

According to the present inventive method, when a tetrafunctional silane is included in the reaction mixture along with the trifunctional silane, the structural rigidity of the product can be improved.

By a tetrafunctional silane is meant sodium silicate, silicic acid, and substituted silicon compounds of the general formula SiX_4 , wherein each X is independently selected from the group consisting of halogen radicals (e.g., chloro, bromo, iodo, etc.). Although the tetrafunctional silane, trifunctional silane, and water can be combined in any order, it is preferred that the tetrafunctional silane and water be combined prior to including the trifunctional silane in the mixture. In water, the tetrafunctional silanes of the present invention can be represented by the general formula $\text{Si}(\text{OH})_x\text{O}_{2-x/2}$, wherein x is a number from 0 to 4, inclusive. According to the method of the present invention, preferred tetrafunctional silanes include SiCl_4 , sodium silicate, and silicic acid. Especially preferred are sodium silicate and silicic acid.

According to the present inventive method, the trifunctional and tetrafunctional silanes can be used in the reaction mixture in any suitable amount and in any suitable ratio. As the ratio of trifunctional silane to tetrafunctional silane increases, the lipophilic silica produced will have increased lipophilicity, but also

increased density and decreased surface area. As the ratio of trifunctional silane to tetrafunctional silane decreases, the lipophilic silica produced will have decreased density and increased surface area, but
5 decreased lipophilicity. Preferred mole ratios of trifunctional silane to tetrafunctional silane in the context of the present inventive method range from about 0.1:1 to about 1000:1. More preferably, the mole ratios will be in a range of from about 0.2:1 to about 10:1, and
10 most preferably, the mole ratios fall within a range of from about 1:1 to about 5:1.

According to a highly preferred embodiment of the present invention, sodium silicate is used as the tetrafunctional silane, and a chlorosilane of general
15 formula RSiCl_3 , wherein R is as previously defined, is used as the trifunctional silane. Sodium silicate can be represented by the general formula $\text{SiO}_2 \cdot x\text{Na}_2\text{O} \cdot y\text{H}_2\text{O}$, wherein x is a number between 0 and 5, and y is a number from 0 to 10, inclusive. A sodium silicate suspension in
20 water is basic, but an aqueous solution containing a chlorosilane, which hydrolyzes according to the following equation, is acidic: $\text{RSiCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{RSi(OH)}_3 + 3\text{HCl}$. Although the sodium silicate and chlorosilane can be combined in any ratio, according to a highly preferred
25 embodiment of the present inventive method, these reagents are combined to provide a mixture that is substantially neutral (i.e., having a pH of from about 5 to about 9). This can be accomplished if the sodium content of the sodium silicate is known, as is generally
30 the case. For example, some of the more common dry forms of sodium silicate (i.e., wherein y is 0) include Na_2SiO_3 ($\text{SiO}_2 \cdot \text{Na}_2\text{O}$), $\text{Na}_6\text{Si}_2\text{O}_7$ ($\text{SiO}_2 \cdot 3/2\text{Na}_2\text{O}$), and $\text{Na}_2\text{Si}_3\text{O}_7$ ($\text{SiO}_2 \cdot 1/3\text{Na}_2\text{O}$). A highly preferred sodium silicate is $\text{SiO}_2 \cdot 1/3.25\text{Na}_2\text{O}$, which contains the highest ratio of
35 silica to sodium for a sodium silicate that is soluble in

water. A substantially neutral reaction mixture can therefore be prepared by mixing the chlorosilane with the sodium silicate in a ratio that provides an approximately equal number of chlorine and sodium atoms therein. For
5 example, a substantially neutral solution can be prepared by mixing methyltrichlorosilane (MTCS) with $\text{SiO}_2 \cdot 1/3.25\text{Na}_2\text{O}$ in a mole ratio of about 4.9:1 (MTCS : $\text{SiO}_2 \cdot 1/3.25\text{Na}_2\text{O}$).

When the present inventive method is conducted in
10 this manner, the process is simplified in that corrosive acids and bases are neutralized in situ, and need not be added separately to the reaction mixture, nor removed after production of the lipophilic silica. This embodiment of the present invention does, however, result
15 in the production of sodium chloride (NaCl) as a reaction by-product, which in some cases is undesirable for disposal reasons. Furthermore, the resulting lipophilic silica contains some residual sodium, which may be undesirable for some applications (e.g., when used as a
20 reinforcing filler for silicone rubber).

In these cases, it is often desirable to use silicic acid ($\text{Si}(\text{OH})_4$) as the tetrafunctional silane in the present inventive method. Silicic acid can be prepared by, for example, passing sodium silicate through an ion-
25 exchange column to remove the sodium ions therefrom. Mixtures of silicic acid and a trifunctional chlorosilane such as MTCS prepared according to the present inventive method generate HCl. This gas has commercial value and can be recovered from the reaction mixture and used in
30 other applications. Furthermore, the organically modified (e.g., lipophilic) silica produced from these reagents is substantially free of contamination from sodium ions.

Mixtures comprising trifunctional silanes of the
35 formula RSiX_3 , defined above, and tetrafunctional silanes

react very rapidly to form silica. Rates of reaction that are too high often prevent good mixing of the reaction mixtures. Insufficient mixing can lead to variability in the character of the produced silica as well as relatively non-homogenous products. Accordingly, it is preferable to add the trifunctional silane slowly to the mixture. Advantageously, the trifunctional silane can be added in a gas stream to a solution of sodium silicate or other tetrafunctional silane. The gas stream can comprise a non-reactive carrier gas, for example, nitrogen, such that the rate of addition of the trifunctional silane to the tetrafunctional silane is slow enough to allow for good mixing. Any suitable rate of addition of the trifunctional silane to the tetrafunctional silane solution can be used as long as a homogenous mixture is obtained during the reaction process. For example, in a batch reaction, the trifunctional silane can be added to the tetrafunctional silane in one minute to about six hours, preferably in about 15 minutes to about one-hour, more preferably, in about 20 minutes to about 30 minutes. In a continuous process, the trifunctional silane would be added at a suitable and comparable rate. Alternatively, the trifunctional silane can be heated to generate a gas vapor, which can be used to deliver the trifunctional silane to the reaction vessel in the absence of a carrier. The concentration of the gas vapor can be controlled by any suitable method and the flow rate can be adapted to any particular and suitable gas concentration.

When a trifunctional silane, e.g., MTCS, is added into a solution of sodium silicate, it is preferable to control or monitor the pH. A solution of sodium silicate will have a pH of about 11.8. As the trifunctional silane is bubbled into the sodium silicate solution the

pH decreases. The final pH is indicative of the mole ratio of trifunctional and tetrafunctional silanes in the reaction mixture. When the desired quantity of trifunctional silanes has been added, as indicated by pH or other indicia (e.g., inferential measurement of trifunctional gas absorption by the sodium silicate mixture), the addition of the carrier gas/trifunctional silane mixture can be stopped, and, if desired, the temperature, pressure or other reaction conditions can be adjusted.

The lipophilicity of the silica produced according to the method of the present invention can be controlled in a number of ways, including: (a) the R group of the trifunctional silane can be varied, (b) the identity and amount of hydrophobing agent(s) used in the reaction can be varied, and (c) the ratio of trifunctional silane to tetrafunctional silane in the reaction mixture can be varied, as described above. For example, the lipophilicity of the silica can be moderately increased by using ethyltrichlorosilane ($\text{CH}_3\text{CH}_2\text{SiCl}_3$) instead of, or in addition to, MTCS, or substantially increased by using tert-butyltrichlorosilane [$(\text{CH}_3)_3\text{CSiCl}_3$] instead of, or in addition to, MTCS. Modifying the R groups of the hydrophobing agent(s) in this manner will have the same effect on lipophilicity, provided one or more hydrophobing agents is included in the reaction mixture. If a hydrophobing agent is not used, the lipophilicity of the silica prepared according to the method of the present invention will be determined by the trifunctional silane, as described above.

If one or more hydrophobing agents is used in the reaction mixture, the amount of each hydrophobing agent included will impact the lipophilicity of the final product. A small percentage of the silanol groups on the surface of the lipophilic silica produced according to

the present inventive method can be capped by using a small quantity of hydrophobing agent(s), while a larger percentage can be capped, thereby further increasing the lipophilicity of the final product, by using a larger
5 quantity of hydrophobing agent(s). When combinations of two or more hydrophobing agents are used, their relative mole ratios can be optimized to provide predetermined rates and levels of treatment.

It is sometimes desirable to use a large excess of
10 the hydrophobing agent(s) (e.g., hexamethyldisiloxane) in order to achieve a phase separation with the aqueous reaction medium, and to thereby partition the silica with a low BET C value silica (i.e., organically modified or lipophilic silica) into the organic phase comprising the
15 hydrophobing agent. Accordingly, the lipophilic silica then can be advantageously separated from hydrophilic byproducts or reactants.

Generally speaking, the preferred total amount of hydrophobing agent(s) present in the reaction mixture is
20 from about 0% to about 20% by weight of the total amount of the trifunctional and tetrafunctional silanes used. More preferably, the amount present is from about 0% to about 10% by weight of the total amount of trifunctional and tetrafunctional silanes, and most preferably from
25 about 0% to about 5% by weight of the total amount of trifunctional and tetrafunctional silanes.

The hydrophobing agent(s), tetrafunctional silane, trifunctional silane, and water can be combined in any order. However, it is preferred that the tetrafunctional
30 silane and water be combined first, followed by the trifunctional silane, and then the hydrophobing agent(s) last.

The organically modified silica can be recovered from the reaction mixture. Any suitable technique can be
35 used to effect such recovery. Since organic solvents

preferably are not used according in the present inventive method, the recovery of the lipophilic silica and the recovery/recycling of the other reactants (i.e., trifunctional silane, tetrafunctional silane, water, and hydrophobing agent(s) (if used)) is greatly simplified. Very often, the organically modified silica particles will phase separate from the solution, allowing for their easy recovery (e.g., by filtration or decanting).

The lipophilic silica particles made in accordance with the method of the present invention will typically be dried after recovery (e.g., isolation) to remove residual solvents. Any suitable drying technique can be utilized, for example, placing the lipophilic silica into an oven.

The method of the present invention can be used to create lipophilic silica particles and powders with a variety of physical properties. For example, lipophilic silica can be prepared with a tap density of less than about 0.05 to more than about 1 g/cm³, a surface area of less than about 5 to more than about 800 m²/g, and a C value of less than about 10 to more than about 100. The lipophilic silica made in accordance with the present inventive method is useful in a wide range of applications, including as fluid thickeners, thermal insulation, anti-caking agents, molecular sieve materials, and reinforcing fillers for silicone and rubber.

The preparation of lipophilic silica using the method of the present invention can be further understood by reference to the following examples. These examples illustrate the present invention but, of course, should not be construed as in any way limiting its scope.

In the following examples organically modified or lipophilic silica is formed in the provided mixture. The organically modified or lipophilic silica is recovered

from the mixture via vacuum filtration and dried in an exhaust for about 90 minutes. The tap density, surface area and C value of the dried organically modified or lipophilic silica can be measured as described below.

5 Measurement of Tap Density: A known mass of the dry powder is transferred to a 10 cm³ graduated cylinder and tapped 40 times by hand. The volume is then noted, and the density is calculated as mass/volume.

Measurement of Surface Area and C Value: The nitrogen adsorption data is obtained using ASAP2000, an automated volumetric gas sorption system made by Micromeritics Corp. (Atlanta, GA). Prior to performing the adsorption experiment, the samples are outgassed at 180 °C to less than 0.003 mm Hg, which typically takes less than 4 hours. For the adsorption experiment, the amount of nitrogen adsorbed at five different relative pressures over the range 0.05 to 0.25 is obtained and analyzed using the Brunauer-Emmett-Teller (BET) model (Gregg et al, "Adsorption, Surface Area and Porosity," p. 285, Academic Press, New York (1991)). The BET model provides the surface area and C value for the silica. A lower C value is indicative of a greater number of hydrophobic groups on the silica.

25 EXAMPLE 1

This example illustrates two embodiments of the present inventive method which are useful in generating organically modified silica.

Nine ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂ and 8.9 wt% Na₂O) was added to 72 ml deionized water while being stirred. This solution had a pH of 11.8. A gaseous mixture with a relatively low partial pressure of methyltrichlorosilane gas in nitrogen was created by bubbling nitrogen through a conical flask containing small glass beads (to increase the surface area of the

gas-liquid interface) and liquid methyltrichlorosilane. The 10 ml/min of the MTCS-nitrogen gas was bubbled through the solution of sodium silicate, with stirring. The solution became cloudy and gelled at pH 9.7. A
5 portion of this gel, when dried in a 150 °C exhaust oven, yielded an organically modified silica powder with a tap density of 0.32 g/ml, a BET surface area of 97 m²/g, and a BET C value of 56. This dried product did not float on water.

10 The remaining gel portion was repeatedly batch washed hourly with deionized water until the sodium ion concentration in the excess wash fluid was undetectable by a sodium probe capable of detecting less than 1 ppm of sodium. Subsequently, the gel was repeatedly washed
15 hourly with isopropanol until the residual concentration of water in the excess wash fluid was less than 0.5 vol%. The isopropanol was removed by batch washing the gel with heptane until the residual concentration of isopropanol in the excess wash fluid was less than 0.5 vol%. Drying
20 this gel at 150 °C in an exhaust oven resulted in a powder with a tap density of 0.21 g/ml, BET surface area of 601 m²/g, and a BET C value of 77. This dried product did not float on water.

25

EXAMPLE 2

This example illustrates an embodiment of the present inventive method which is useful in generating organically modified silica.

Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂
30 and 8.9 wt% Na₂O) was added to 48 ml of deionized water while being stirred. The pH of the mixture was 11.8. Thirty ml/min of methyltrichlorosilane-nitrogen gas (see Example 1) was bubbled through the stirred solution. The solution became cloudy and gelled at pH 8.2. The gel was

batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable by a sodium probe capable of detecting less than 1 ppm of sodium. Subsequently, the gel was repeatedly batch
5 washed with isopropanol until the residual concentration of water in the excess wash fluid was less than 0.5 vol%. This was followed by repeated hourly washing of the gel with heptane until the residual concentration of isopropanol in the excess wash fluid was less than 0.5
10 vol%. Drying this gel at 150 °C in an exhaust oven resulted in a powder with a tap density of 0.20 g/ml, BET surface area of 741 m²/g, and a BET C value of 64. This dried product did not float on water.

15

EXAMPLE 3

This example illustrates an embodiment of the present inventive method which is useful in generating organically modified silica.

Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂
20 and 8.9 wt% Na₂O) was added to 72 ml of deionized water while being stirred. The pH of the mixture was 11.8. Fifty ml/min of methyltrichlorosilane-nitrogen gas (see Example 1) was bubbled through the stirred solution until the solution reached pH 2.6. The reaction vessel was
25 sealed and heated to 65 °C in an oven. A gel formed within fifteen hours, which then was repeatedly batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable by a sodium probe capable of detecting less than 1 ppm of
30 sodium. Subsequently, the gel was repeatedly batch washed with isopropanol until the residual concentration of water in the excess wash fluid was less than 0.5 vol%. This was followed by repeated hourly washing of the gel with heptane till the residual concentration of

isopropanol in the excess wash fluid was less than 0.5 vol%. Drying this gel at 150 °C in an exhaust oven resulted in a powder with a tap density of 0.64 g/ml, BET surface area of 858 m²/g, and a BET C value of 296. This
5 dried product did not float on water.

EXAMPLE 4

This example illustrates an embodiment of the present inventive method which is useful in generating
10 organically modified silica.

Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂ and 8.9 wt% Na₂O) was added to 48 ml of deionized water while being stirred. The pH of the mixture was 11.8. Eighty ml/min of methyltrichlorosilane-nitrogen gas (see
15 Example 1) was bubbled through the stirred solution until the solution reached pH 1.5. The reaction vessel was sealed and heated to 65 °C in an oven. A gel formed within fifteen hours, which then was repeatedly batch washed with deionized water until the sodium ion
20 concentration in the excess wash fluid was undetectable by a sodium probe capable of detecting less than 1 ppm of sodium. Subsequently, the gel was repeatedly batch washed with isopropanol until the residual concentration of water in the excess wash fluid was less than 0.5 vol%.
25 This was followed by repeated batch washing of the gel with heptane until the residual concentration of isopropanol in the excess wash fluid was less than 0.5 vol%. Drying this gel at 150 °C in an exhaust oven resulted in a powder with a tap density of 0.29 g/ml, BET
30 surface area of 852 m²/g, and a BET C value of 254. This dried product did not float on water.

EXAMPLE 5

This example illustrates an embodiment of the present inventive method which is useful in generating organically modified silica.

- 5 Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO_2 and 8.9 wt% Na_2O) was added to 48 ml of deionized water while being stirred. The pH of the mixture was 11.8. Eighty ml/min of methyltrichlorosilane-nitrogen gas (see Example 1) was bubbled through the stirred solution until
10 the solution pH was less than zero. The reaction vessel was sealed and heated to 65 °C in an oven. A gel formed within fifteen hours, which then was repeatedly batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable
15 by a sodium probe capable of measuring less than 1 ppm of sodium. Subsequently, the gel was repeatedly batch washed with isopropanol until the residual concentration of water in the excess wash fluid was less than 0.5 vol%. This was followed by repeated batch washing of the gel
20 with heptane until the residual concentration of isopropanol in the excess wash fluid was less than 0.5 vol%. Drying this gel at 150 °C in an exhaust oven resulted in a powder with a tap density of 0.38g/ml, BET surface area of 817 m^2/g , and a BET C value of 56. This
25 dried product did not float on water.

EXAMPLE 6

- This example illustrates an embodiment of the present inventive method which is useful in generating
30 lipophilic silica.

Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO_2 and 8.9 wt% Na_2O) was added to 48 ml of deionized water while being stirred. The pH of this mixture was 11.8. Fifteen ml/min of methyltrichlorosilane-nitrogen gas (see

Example 1) was bubbled through the stirred solution. The solution became cloudy and gelled at pH 9.4. The gel was repeatedly batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable by a sodium probe capable of detecting less than 1 ppm of sodium. Two volumes of deionized water were added to one volume of the washed gel and aged at 65 °C in a sealed reaction vessel in an oven for 1 hour. The excess water was then drained from the gel and two volumes of trimethylchlorosilane were added to one volume of the gel. Within one hour, the gel became hydrophobic and partitioned into a non-aqueous phase (the top phase) from an aqueous phase (the bottom phase). The nonaqueous phase was drained from the gel, which was dried at 150 °C in an exhaust oven. This yielded a powder with a tap density of 0.11 g/ml, a BET surface area of 583 m²/g, and a BET C value of 14. This dried product floats on water for more than 200 hours.

20

EXAMPLE 7

This example illustrates an embodiment of the present inventive method which is useful in generating lipophilic silica.

Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂ and 8.9 wt% Na₂O) was added to 48 ml of deionized water while being stirred. The pH of this mixture was 11.8. Fifteen ml/min of methyltrichlorosilane-nitrogen gas (see Example 1) was bubbled through the stirred solution until the solution reached pH 1.8. The vessel was sealed and heated in an oven to 65 °C. A gel formed within fifteen hours. The gel then was repeatedly batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable with a sodium probe capable of detecting less than 1 ppm sodium. Excess

water was drained from the gel and two volumes of trimethylchlorosilane were added to one volume of the gel. Within one hour, the gel became hydrophobic and partitioned into a non-aqueous phase (the top phase) from an aqueous phase (the bottom phase), which was dried at 150 °C in an exhaust oven. The non-aqueous phase was drained providing a powder with a tap density of 0.14 g/ml. This dried product floats on water for more than 200 hours.

10

EXAMPLE 8

This example illustrates an embodiment of the present inventive method which is useful in generating lipophilic silica.

15 Six ml of sodium silicate (PQ Grade N: 28.7 wt% SiO₂ and 8.9 wt% Na₂O) was added to 48 ml of deionized water while being stirred. The pH of this mixture was 11.8. Eighty ml/min of methyltrichlorosilane-nitrogen gas (see Example 1) was bubbled through the stirred solution until
20 the solution reached pH 1.8. The reaction vessel was sealed and heated in an oven to 65 °C. A gel formed within fifteen hours. The gel then was repeatedly batch washed with deionized water until the sodium ion concentration in the excess wash fluid was undetectable
25 by a sodium probe capable of detecting less than 1 ppm. Two volumes of deionized water were added to one volume of the washed gel and aged in a sealed vessel at 65 °C in an oven for 20 hours. The excess water was then drained from the gel, and two volumes of trimethylchlorosilane
30 were added to one volume of the gel. Within one hour, the gel became hydrophobic and partitioned into a non-aqueous phase (the top phase) from an aqueous phase (the bottom phase), which was dried at 150 °C in an exhaust oven. The non-aqueous phase was drained providing a

powder with a tap density of 0.06 g/ml, BET surface area of 737 m²/g, and a BET C value of 14. This dried product floats on water for more than 200 hours.

5

All of the references cited herein, including patents, patent applications, and publications, are hereby incorporated in their entireties by reference.

While this invention has been described with an
10 emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this
15 invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

WHAT IS CLAIMED IS:

1. A method of preparing organically modified silica comprising:
 - 5 (a) providing a mixture consisting essentially of:
 - (i) at least one organically modified silica precursor selected from the group consisting of trifunctional silanes of the general formula RSiX_3 ,
10 wherein R is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less and phenyl radicals, and each X is independently selected from the group consisting of halogen radicals and hydroxyl radicals and
15 salts thereof,
 - (ii) water, and
 - (iii) at least one tetrafunctional silane selected from the group consisting of silica, sodium silicate, and silanes of the formula SiX_4 , wherein each X
20 is independently selected from the group consisting of halogen radicals,
 - (b) allowing said organically modified silica to form in said mixture, and
 - (c) recovering said organically modified silica
25 from said mixture.
2. The method of claim 1, wherein said organically modified silica precursor is methyltrichlorosilane.
3. The method of claim 1, wherein said
30 tetrafunctional silane is selected from the group consisting of sodium silicate, silicic acid, and tetrachlorosilane.
4. The method of claim 2, wherein said
tetrafunctional silane is selected from the group consisting of sodium silicate, silicic acid, and
35 tetrachlorosilane.

5. The method of claim 4, wherein said tetrafunctional silane is sodium silicate.

6. The method of claim 5, wherein the pH of said mixture is from about 4 to about 9.

5 7. The method of claim 6, wherein the quantities of said methyltrichlorosilane and said sodium silicate are chosen to provide an approximately equal number of chlorine atoms and sodium atoms in said mixture.

8. The method of claim 1, wherein said water and
10 said tetrafunctional silane are combined prior to adding said organically modified silica precursor.

9. The method of claim 1, wherein said mixture further comprises at least one hydrophobing agent
selected from the group consisting of monofunctional
15 silanes of the general formula R_3SiX , a bifunctional silane of the general formula R_2SiX , cyclic siloxanes of the general formula $(R_2SiO)_y$, and linear siloxanes of the general formula $R'_3Si-O-(Si(R_2)-O)_z-SiR'_3$, wherein each R' is independently selected from the group consisting of
20 aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less, phenyl radicals, and hydroxyl radicals, each R is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less and phenyl radicals, X
25 is selected from the group consisting of halogen radicals, y is 3 or 4, and z is an integer from 0 to 10, inclusive.

10. The method of claim 9, wherein said hydrophobing agent is selected from the group consisting
30 of monofunctional silanes of the general formula $(R'')_3SiX$, wherein R'' is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less.

11. The method of claim 9, wherein said
35 hydrophobing agent is selected from the group consisting

of trimethylchlorosilane, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, hexamethylcyclotrisiloxane, hydroxy terminated polydimethylsiloxane, and octamethylcyclotetrasiloxane.

5 12. The method of claim 9, wherein said water and said tetrafunctional silane are combined prior to adding said organically modified silica precursor.

10 13. The method of claim 12, wherein said water, said tetrafunctional silane, and said lipophilic silica precursor are combined prior to adding said hydrophobing agent.

14. The method of claim 1, wherein said method is performed in the absence of an organic cosolvent.

15 15. The method of claim 9, wherein said method is performed in the absence of an organic cosolvent.

16. The method of claim 1, wherein said recovering of said organically modified silica in step (c) comprises adding at least one hydrophobing agent selected from the group consisting of monofunctional silanes of the general
20 formula R_3SiX , a bifunctional silane of the general formula R_2SiX , cyclic siloxanes of the general formula $(R_2SiO)_y$, and linear siloxanes of the general formula $R'_3Si-O-(Si(R_2)-O)_z-SiR'_3$, wherein each R' is independently selected from the group consisting of
25 aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less, phenyl radicals, and hydroxyl radicals, each R is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less and phenyl radicals, X
30 is selected from the group consisting of halogen radicals, y is 3 or 4, and z is an integer from 0 to 10, inclusive.

17. The method of claim 16, wherein said hydrophobing agent is selected from the group consisting
35 of monofunctional silanes of the general formula

$(R'')_3SiX$, wherein R'' is independently selected from the group consisting of aliphatic hydrocarbon and fluorocarbon radicals of 6 carbon atoms or less.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/00157

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09C1/30 C01B33/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09C C01B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 35 25 B02 A (BAYER AG) 22 January 1987 see the whole document ---	1-6, 8-12, 14, 15
X	GB 1 062 599 A (DEUTSCHE GOLD-UNO SILBER SCHEIDEGANSTALT) 22 March 1967 see claims 1, 2, 5 see page 1, line 56 - page 2, line 23 see page 2, line 47 - line 3 see examples 1-3 ---	1-6, 8, 14
X	US 2 802 850 A (JOHN W. WETZEL) 13 August 1957 see the whole document --- <div style="text-align: center;">-/--</div>	1-6, 8
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">29 April 1999</div>		Date of mailing of the international search report <div style="text-align: center;">10/05/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3018		Authorized officer <div style="text-align: center;">Rigondaud, B</div>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00157

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 208 316 A (BOOE RUOLF ET AL) 17 June 1980</p> <p>see claim 2 see column 2, line 45 - column 3, line 20 see examples 2,4 ---</p>	<p>1,3, 9-11, 14-17</p>
A	<p>US 2 589 705 A (SAMUEL S. KISTLER) 18 March 1952</p> <p>see the whole document ---</p>	<p>1,2, 9-11,14, 15</p>
A	<p>US 4 644 077 A (GUPTA GOUTAM) 17 February 1987</p> <p>see the whole document ---</p>	<p>1,2</p>
A	<p>G8 1 110 331 A (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT) 18 April 1968</p> <p>see claims 1,2 see page 2, line 94 - line 112 ---</p>	<p>1,2</p>
A	<p>US 5 013 585 A (SHIMIZU TAKAAKI ET AL) 7 May 1991</p> <p>see claim 1 ---</p>	<p>1,2</p>
A	<p>OE 20 65 572 A (DEGUSSA) 4 July 1974</p> <p>see the whole document ---</p>	<p>1,9</p>
P,A	<p>WO 98 45210 A (CASOT CORP) 15 October 1998</p> <p>see claims 1,8,9,12,17-20 see page 2, line 13 - line 27 see page 4, line 4 - line 9 see page 12, line 12 - page 13, line 6 see page 15, line 9 - line 28 see page 22, line 24 - page 24, line 7 ---</p>	<p>1</p>
A	<p>DE 44 19 234 A (WACKER CHEMIE GMBH) 7 December 1995 -----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/00157

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3525802 A	22-01-1987	NONE	
GB 1062599 A		8E 641508 A OE 1229504 8 FR 1374847 A NL 300549 A US 2786042 A	16-04-1964 19-03-1957
US 2802850 A	13-08-1957	NONE	
US 4208316 A	17-06-1980	NONE	
US 2589705 A	18-03-1952	NONE	
US 4644077 A	17-02-1987	BR 8603582 A CA 1251695 A EP 0216047 A JP 1920169 C JP 6047457 8 JP 62072515 A	22-04-1987 28-03-1989 01-04-1987 07-04-1995 22-06-1994 03-04-1987
GB 1110331 A		FR 1429104 A	05-05-1966
US 5013585 A	07-05-1991	NONE	
OE 2065572 A	04-07-1974	NONE	
WO 9845210 A	15-10-1998	AU 6894898 A	30-10-1998
OE 4419234 A	07-12-1995	AT 169948 T AU 669647 8 AU 2037595 A BR 9502619 A CA 2149821 A CN 1121044 A DE 59503235 0 EP 0686676 A ES 2121261 T FI 952622 A JP 7330324 A NO 952158 A US 5686054 A US 5851715 A	15-09-1998 13-06-1996 04-01-1996 02-01-1996 02-12-1995 24-04-1996 24-09-1998 13-12-1995 16-11-1998 02-12-1995 19-12-1995 04-12-1995 11-11-1997 22-12-1998